

PATENT SPECIFICATION

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(54) IMPROVED FLUORESCENT DYE COLORED VINYL CHLORIDE HOMOPOLYMERS AND COPOLYMERS

(71) We, HERCULES INCORPORATED, a corporation organized under the laws of the State of Delaware, one of the United States of America, of 910 Market Street, City of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fluorescent colored plastics. More particularly, it relates to vinyl chloride homopolymers and copolymers containing an organic fluorescent dye for the coloration thereof.

Polyvinyl chloride (PVC) and vinyl chloride copolymers are in common commercial use. A form of such resin which does not contain plasticizers and is commonly referred to as "rigid" PVC, even if it comprises a vinyl chloride copolymer, is encountered frequently and may be in a sheet or film form. This resin is used in its clear form but it is often desired to color the resin with a suitable dye or pigment. In the present context, reference is made to rigid vinyl chloride homopolymers and copolymers having a fluorescent appearance which is imparted by the addition of an organic fluorescent dye, as distinguished from a pigment, which is dispersed through the PVC resin.

The present invention provides improvements in organic fluorescent dye colored rigid vinyl chloride homopolymers and copolymers by way of enhanced initial fluorescent appearance of the product and by way of improvements in the resistance of the dye to fading upon exposure to light such as sunlight. In accordance with the present invention it has

been discovered that these improvements can be achieved by combining as by blending a chlorinated polyethylene with the vinyl chloride homopolymer or copolymer so that the chlorinated polyethylene constitutes from 9 to 90% by weight of the blend thereof with the vinyl chloride homopolymer or copolymer. If desired, additional improvement in fluorescent appearance and fade resistance can be achieved if certain vinyl resin stabilizers are added to the formulation. To this end it has been found that a non-mercaptide organo tin or a barium-cadmium-zinc or a strontium-zinc compound can be used as stabilizer, the latter two categories of stabilizer preferably being used in combination with a chelator. The use of such stabilizers will provide surprisingly superior results than can be obtained with other types of vinyl resin stabilizer.

Best results have been obtained where the organic fluorescent dye is a rhodamine dye such as rhodamine B base, although other organic fluorescent dyes and combinations thereof are contemplated. In the preferred embodiment, the improved product is formed in a sheet or film form and the advantages of the invention will be demonstrated in relation thereto in the examples given herein-after.

The product containing chlorinated polyethylene and, optionally, vinyl stabilizers is processed and formulated in accordance with conventional techniques used with vinyl chloride homopolymers and copolymers. Thus, the end product will usually contain in addition to a vinyl chloride homopolymer or copolymer, chlorinated polyethylene, and possibly a vinyl stabilizer, a conventional processing resin which aids in the manipulation of the materials in forming the end physical

product sought. Also, conventional lubricants may be utilized for their expected benefits as well as ultraviolet screening compounds.

- 5 The invention contemplates the use of any vinyl chloride homopolymer in any of the variations normally encountered. In addition, copolymers of vinyl chloride may be used with similar benefits including such copolymers as vinyl chloride/vinyl acetate, vinyl chloride/propylene, and vinyl chloride/ethylene copolymers.

- 10 The chlorinated polyethylene used in combination with the vinyl chloride homopolymer or copolymers may be any of those materials of this type which are referred to as impact modifiers. The benefits of the invention are obtained by combining an amount of chlorinated polyethylene sufficient to improve the fluorescence and fade resistance of the colored end product. It has been found that the chlorinated polyethylene should constitute 9—90% by weight of the total weight of the vinyl chloride copolymer or homopolymer and the chlorinated polyethylene. Best results are obtained where the chlorinated polyethylene constitutes 20—70% by weight of this polymer mixture and most preferably where the chlorinated polyethylene constitutes 25—45%

by weight of the polymer mixture. Useful chlorinated polyethylenes may fall in a broad range of materials having differing chlorine content. Best results have been observed where the polyethylene has a chlorine content of 35—40% by weight.

Where a vinyl stabilizer of the specified type is employed, it will generally be included to be an amount of 1—5% of the weight of the vinyl chloride homopolymer or copolymer content, preferably 2—3% by weight. The fluorescent dye will generally be present in an amount of 0.05—.5% by weight of the vinyl chloride homopolymer or copolymer content and preferably .2—.3% by weight, although all of these amounts may be varied to some extent depending upon the particular formulation and use of the end product.

To illustrate the invention, a series of experiments were performed using the following materials and procedures. Although the experiments involve a sheet form of product, it will be appreciated that the resins could be used to make articles or parts by casting or molding in conventional fashion. Whatever the physical form of the end product, the same advantages in fluorescence and fade resistance will be obtained.

TABLE I

Trade Name	PVC 40	Geon* 400×47	Cumberland 470	QSQH
Supplier	Diamond-Shamrock Chemical Co.	B.F. Goodrich Chemical Co.	Air Reduction Co.	Union Carbide Chemical Co.
Type	Polyvinyl Chloride	Vinyl Chloride/Vinyl Acetate Copolymer	Vinyl Chloride/Propylene Copolymer	Vinyl Chloride/Ethylene Copolymer
Approx. Monomer Ratio	100/0	90/10	90/10	—
Specific Gravity	1.390	1.360	1.352	—
Inherent Viscosity ASTM 1243-58T Method A (Typical Values)	0.80	0.62	0.60	—

* Geon is a Registered Trade Mark.

Impact Modifiers

- 60 (1) Acrylic Terpolymer (Butadiene/Styrene/Methyl methacrylate Acryloid 6721—Rohm & Haas Company Now known as Acryloid KM611)
- 65 (2) Chlorinated Polyethylene Tyrin QX2243.16—Dow Chemical Company Now known as Dow CPE3614 (Dow is a Registered Trade Mark).

Processing Resin

- (1) Acryloid K120N Poly Methyl Methacrylate—Rohm & Haas Company

Stabilizers

- (1) Organo Tin Carboxylate—Advastab T150
- (2) Tin Mercaptide—Advastab T17M (Advastab is a Registered Trade Mark)

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Advance Division, Carlisle Chemical Works, Inc.

- (3) Strontium-Zinc Compound Mark E in combination with a chelating agent, Triphenyl Phosphite-Mark C Argus Chemical Division, Witco Chemical Company

- (4) Epoxidized Soya Oil Paraplex G—62—Rohm & Haas Company (Paraplex is a Registered Trade Mark).

Lubricants

- (1) Stearic Acid—Triple Pressed CP Hall Company

- (2) Propylene Glycol Monostearate or Polyethylene Glycol Monostearate Technical Grade Nopco Division, Diamond Shamrock In combination with oxidized low molecular weight Polyethylene—AC 629A—Allied Chemical Company

Ultraviolet Screens

- (1) Tinuvin P—Geigy Chemical Company 2(2-Hydroxy-5 Methylphenyl) benzotriazole (Tinuvin is a Registered Trade Mark).

Colorant

- (1) Rhodamine B Base—American Cyanamid Company (Lot MR 311—14)

The compositions were weighed in batch sizes totaling approximately 350 grams using methods having accuracy of three significant figures.

The weighted components were placed in polyethylene bags. The open end of the bag was twisted to seal in air to form a spherical balloon permitting rotational shaking agitation to produce a uniformly mixed dry blended composition.

The dry blended composition was then mixed in the nip of a two roll 8"×16" laboratory mill heated to 330°F.—340°F. and milled for 5 minutes after the composition had fused and banded on the mill roll. The mill roll peripheral speed ratio was 1.16. To guarantee uniform mixing, the stock was

continuously cut from one side of the mill to the other and "end rolled" three times on and off the mill. The mill sheets were sheeted off at approximately .040" thickness.

Samples were cut from the mill sheets and pressed for one minute at 350°F. between chromed ferrotype plates to produce test specimens of .004" and .012" thickness.

Test thickness tolerances were .0040"—.0045" and .0120"—.0125". For exposure testing $\frac{3}{4}$ "×2 $\frac{3}{4}$ " strips were cross mounted on window type flat aluminium frames (.032" thickness) with open window dimensions 1 $\frac{3}{4}$ "×5". The samples were attached to the exposure frames with cloth backed adhesive tape.

The samples were exposed at Desert Sunshine Exposure Tests, 7740 North 15th Avenue, Phoenix, Arizona.

The frames were mounted in the outdoor accelerated weathering unit—EMMA, and returned after 25,000, 50,000, 75,000 and 100,000 Langley's exposure.

EMMA, Equatorial Mount with Mirrors for Acceleration, is a test exposure unit that moves with the sun and focuses the sunlight onto the test sample by means of special finish aluminium reflecting panels. The reflection amounts to 70—80% of the ultraviolet radiation and 85% of the visible. The radiation impinging on the sample is measured in gram calories per square centimeter (Langley's).

The samples before and after aging are checked in a spectroradiometer for light transmission at 625 m μ using a mercury vapor light source (Penray Lamp).

The characteristics of the light source show no emission peaks at 625 m μ . Therefore, spectroradiometer readings at this wavelength 625 m μ . result from fluorescence—shifted energy from the shorter end of the spectrum.

Hence, the light stability of each compound can be studied by following the decay of fluorescence at 625 m μ .

The results are shown in the following Tables II, III and IV in which all parts shown are by weight.

TABLE II
Effect of Type of Vinyl Chloride Homo-or Copolymer
.004" Test Samples*

Sample No.	1	2	3	4
PVC 40 Homopolymer	100.0			
Geon 400×47 (Vinyl Chloride/ Vinyl Acetate Copolymer)		100.0		
Cumberland 470 (Vinyl Chloride/ Propylene Copolymer)			100.0	
QSQH (Vinyl Chloride/Ethylene Copolymer)				100.0
Dow CPE 3614	10.0	10.0	10.0	10.0
Acryloid K120N	5.0	5.0	5.0	5.0
Advastab T150	3.0	3.0	3.0	3.0
Paraplex G-62	3.0	3.0	3.0	3.0
Stearic Acid	0.5	0.5	0.5	(*)
Tinuvin P	2.0	2.0	2.0	2.0
20 Rhodamine B Base	0.227	0.227	0.227	0.227

* Each sample was lubricated with 1.0 part of propylene glycol monostearate in combination with 0.5 part of oxidized low molecular weight polyethylene (AC 629A).

Spectroradiometer Readings—Fluorescence Decay

Original	61	56	59	64
After exposure to 100,000 Langley's	46	42	42	47
% Original	76	75	71	74

The above results show that the invention is applicable to vinyl chloride homopolymer as well as copolymers thereof.

TABLE III
Effect of the Impact Modifier

.004" Test Samples

Sample No.	1	2	3	4	5	6
PVC 40 Homopolymer	100.0	100.0				
Geon 400 × 47 (Vinyl Chloride/Vinyl Acetate Copolymer)			100.0	100.0		
Cumberland 470 (Vinyl Chloride/Propylene Copolymer)					100.0	100.0
Acryloid 6721	10.0		10.0		10.0	
Dow CPE 3614		10.0		10.0		10.0
Acryloid K120N	5.0	5.0	5.0	5.0	5.0	5.0
Advastab T150	3.0	3.0	3.0	3.0	3.0	3.0
Paraplex G-62	3.0	3.0	3.0	3.0	3.0	3.0
Stearic Acid	0.5	0.5	0.5	0.5	0.5	0.5
Tinuvin P	2.0	2.0	2.0	2.0	2.0	2.0
Rhodamine B Base	0.227	0.227	0.227	0.227	0.227	0.227
Spectroradiometer Readings—Fluorescence Decay						
Original	51	61	49	56	46	59
After exposure to 100,000 Langleys	15	46	17	42	16	42
% Original	29	76	35	75	35	71

The above results show that formulations containing chlorinated polyethylene show consistent superiority over formulations containing other types of impact modifiers such as acrylic with respect to initial fluorescence and color retention. In each of the above systems

containing chlorinated polyethylene the spectroradiometer readings were substantially initially higher and maintained 36—47% more fluorescence after 100 M. Langleys exposure as compared with the formulations containing the acrylic modified formulations.

TABLE IV
Effect of Type of Stabilizer

.004" Test Samples									
Sample No.	1	2	3	4	5	6	7	8	9
PVC 40 Homopolymer	100.0	100.0	100.0						
Geon 400×47 (Vinyl Chloride/Vinyl Acetate Copolymer)				100.0	100.0	100.0			
Cumberland 470 (Vinyl Chloride/Propylene Copolymer)							100.0	100.0	100.0
Dow CPE 3614	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Acryloid K120N	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Paraplex G-62	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Stearic Acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Tinuvin P	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Rhodamine B Base	0.227	0.227	0.227	0.227	0.227	0.227	0.227	0.227	0.227
Advastab T17M (Tin Mercaptide)	2.0			2.0			2.0		
Mark E/Mark C Strontium Zinc/Chelator		3/1			3/1			3/1	
Advastab T150 Tin Carboxylate			3.0			3.0			3.0
Spectroradiometer Readings—Fluorescence Decay									
Original	45	72	61	51	69	56	54	73	59
After exposure to 100M. Langley's	14	47	46	34	43	42	33	40	42
% Original	31	65	76	67	63	75	61	55	71

5 The above results show the uniqueness of vinyl stabilizers contemplated by this invention. The sulfur-containing tin mercaptide stabilizer performed consistently more poorly than strontium zinc compound/chelator or tin carboxylates with respect to fluorescence after exposure.

The following experimental work is

designed to show the effect of the concentration of chlorinated polyethylene in the formulation as well as the effect of the percentage by weight of chlorine in the chlorinated polyethylene polymer. The results are illustrated in Figs. 1—4 of the accompanying drawings. 15 The results shown in Figs. 1—4 were attained with the following formulation:

		Part by Weight	65
	PVC 40	100—X	
	Chlorinated Polyethylene	X	
5	Acryloid K120N	5.0	
	Advastab T150	3.0	
	Strontium-zinc compound Mark E in combination with a chelating agent, triphenyl phosphate—		
10	Mark C	3.0/1.0	
	Paraplex G62	5.0	
	Polyethylene Glycol Mono- stearate	1.0	
	Low M.W. Polyethylene AC629A	0.5	
15	Tinuvin P	2.0	
	Rhodamine B base (MR961—1)	0.227	

Masterbatches of the base compounds were made using 100% PVC 40 and the two 100% chlorinated polyethylene polymers with the two stabilization systems each, making a total of six masterbatches.

The masterbatches were mixed five minutes at 330—340°F. on a two roll mill, sheeted off and cooled.

Blends of the masterbatches were then milled together in the proper proportion for three minutes and sheeted off for lab pressing.

The milled compounds were pressed between ferrotype plates to 4 mils (.004") and mounter in exposure frames as described in the preceding experiments. Spectroradiometer readings before and after exposure were taken and the results plotted on bar graphs showing the decay of fluorescence of the various blends as follows:

Fig. 1 represents a blend of Diamond-Shamrock Chemical Company's PVC 40 and Dow Chemical Company's chlorinated polyethylene CPE 3614. The percentage by weight of chlorine in this polymer is 36% by weight. The formulation represented by results in Fig. 1 utilized Advastab T150 (tin carboxylate) vinyl stabilizer.

Fig. 2 utilizes the same formulation as used in obtaining the data for Fig. 1 except that the vinyl stabilizer was strontium-zinc compound Mark E in combination with a chelating agent, triphenyl phosphite, Mark C.

Fig. 3 was obtained from a formulation using a polymer blend of Diamond-Shamrock Chemical Company's PVC 40 with Dow Chemical Company's chlorinated polyethylene CPE 2243.25 which has a chlorine content of 48% by weight. The vinyl stabilizer was Advastab T150 (tin carboxylate).

Fig. 4 utilized the same polyethylene mixture as in Fig. 3, the only difference being the use of strontium-zinc compound Mark E in combination with a chelating agent, triphenyl phosphate, Mark C. (vinyl stabilizer) instead of Advastab T150.

WHAT WE CLAIM IS:—

1. A blended organic fluorescent dyed rigid polyvinyl chloride or vinyl chloride copolymer

containing resin which additionally contains 9—90% by weight of chlorinated polyethylene based on the total weight of the polyvinyl chloride or vinyl chloride copolymer and chlorinated polyethylene.

2. A resin in accordance with claim 1 in which said chlorinated polyethylene constitutes from 20—70% by weight of the total weight of the polyvinyl chloride or vinyl chloride copolymer and the chlorinated polyethylene.

3. A resin in accordance with claim 2, in which said chlorinated polyethylene constitutes from 25—45% by weight of the total weight of the polyvinyl chloride or vinyl chloride copolymer and the chlorinated polyethylene.

4. A resin in accordance with any one of the preceding claims which contains a vinyl resin stabilizer selected from non-mercaptide organo tin, barium-cadmium-zinc, and strontium-zinc compounds.

5. A resin in accordance with claim 4, wherein the barium-cadmium-zinc or strontium-zinc compound is present together with a chelator.

6. A resin in accordance with claim 4, wherein the non-mercaptide organo-tin is a tin carboxylate.

7. A resin in accordance with any one of claims 4 to 6 which contains from 1 to 5% by weight of the stabilizer based on the content thereof of polyvinyl chloride or vinyl chloride copolymer.

8. A resin in accordance with claim 7, which contains from 2 to 3% by weight of the stabilizer based on the content thereof of polyvinyl chloride or vinyl chloride copolymer.

9. A resin in accordance with any one of the preceding claims, in which said copolymer is selected from vinyl chloride/vinyl acetate copolymer, vinyl chloride/propylene copolymer, and vinyl chloride/ethylene copolymer.

10. A resin in accordance with any one of the preceding claims in which said chlorinated polyethylene contains from 35 to 40% by weight of chlorine therein.

11. A resin in accordance with any one of the preceding claims, which contains a lubricant, a resinous processing aid, and a UV screen.

12. A resin in accordance with any one of the preceding claims, in which said organic fluorescent dye is a rhodamine dye.

13. A resin in accordance with claim 12 in which said dye is rhodamine B base.

14. A resin in accordance with any one of the preceding claims, in which said organic fluorescent dye comprises a combination of dyes.

15. A resin in accordance with any one of the preceding claims in which said dye is present in an amount of from .05 to .5% by weight of the content thereof of polyvinyl chloride or vinyl chloride copolymer.

16. A resin in accordance with claim 15, in which said dye is present in an amount of

from .2 to .3% by weight of the content thereof of polyvinyl chloride or vinyl chloride copolymer.

- 5 17. An organic fluorescent dyed rigid resin as claimed in claim 1 substantially as described herein with reference to any one of the accompanying drawings.

- 10 18. An organic fluorescent dyed rigid resin as claimed in claim 1 substantially as described in any one of the foregoing Tables II, III and IV.

19. A shaped article whenever prepared from the resin of any one of claims 1 to 18.

20. An article in accordance with claim 19, which is a cast, moulded, or formed sheet.

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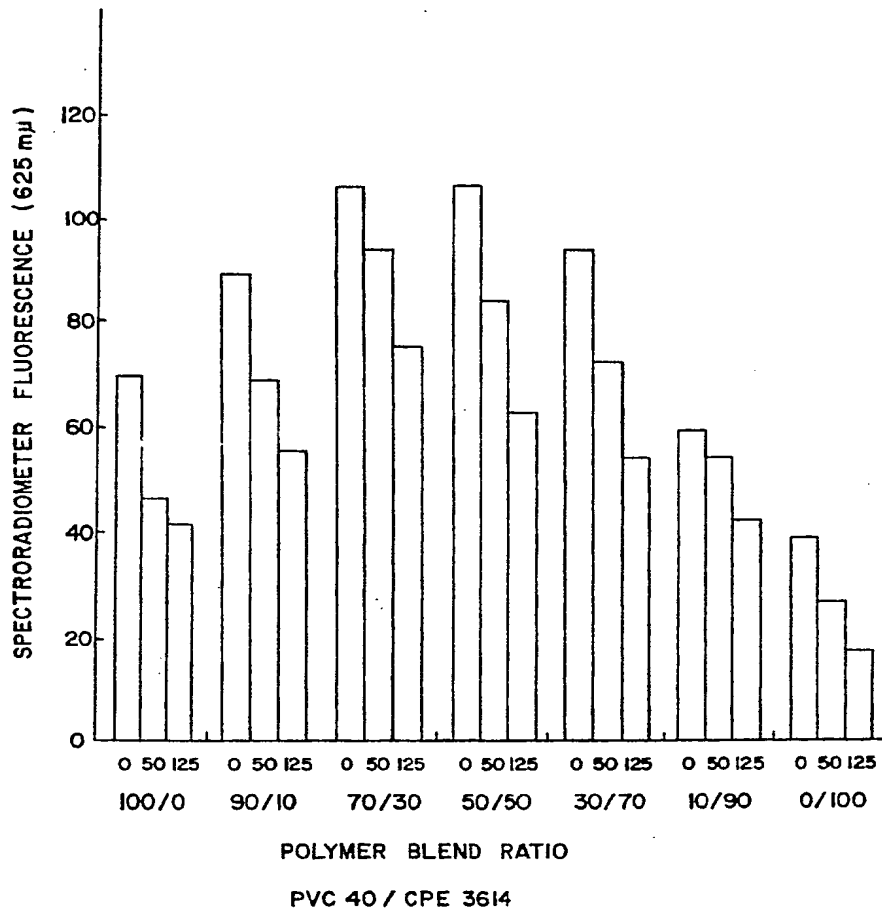
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FLUORESCENCE DECAY VS EMMA EXPOSURE
0-50,000-125,000 LANGLEYS



FIG_1

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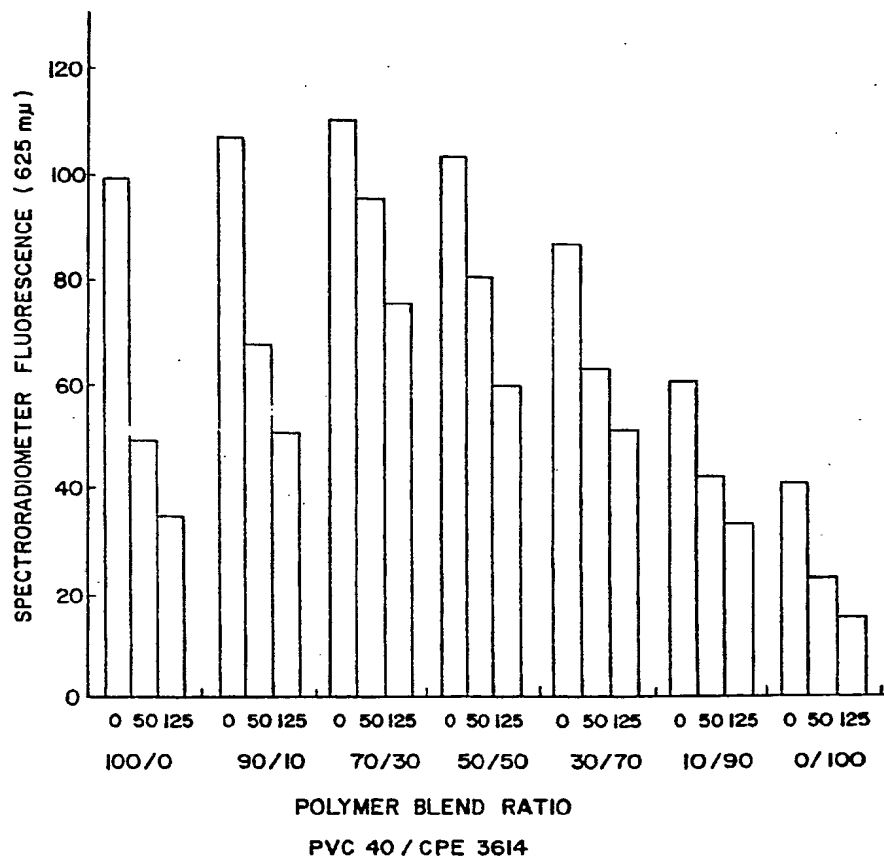
COMPLETE SPECIFICATION

4 SHEETS

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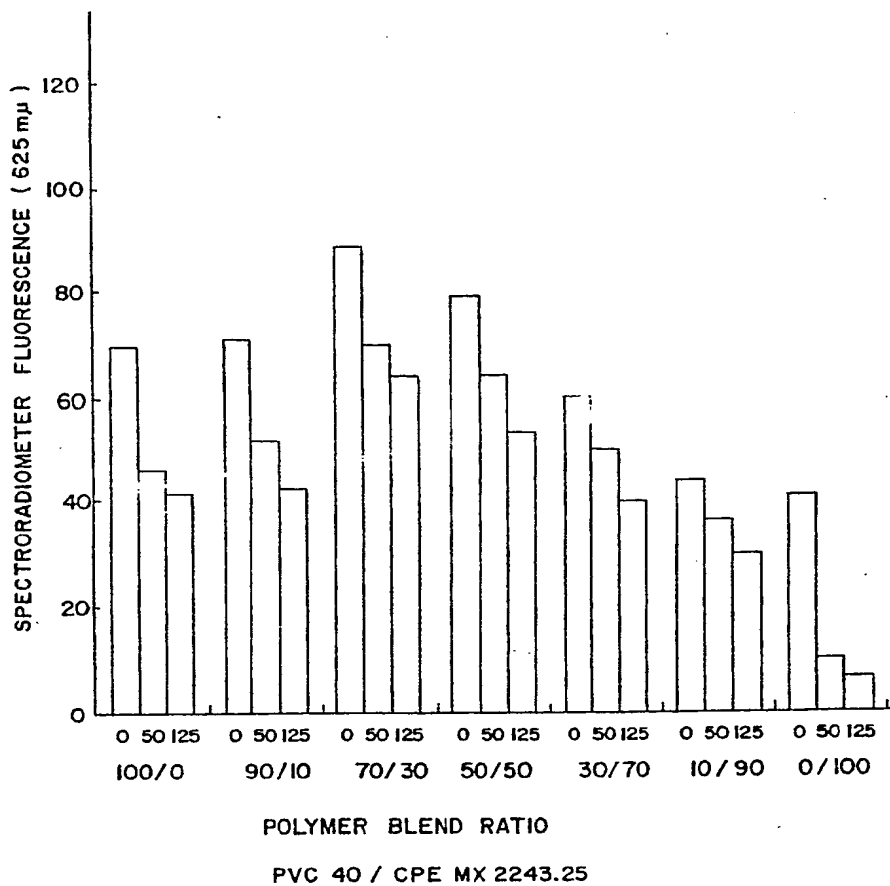
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FLUORESCENCE DECAY VS EMMA EXPOSURE
0-50-125 THOUSAND LANGLEYS



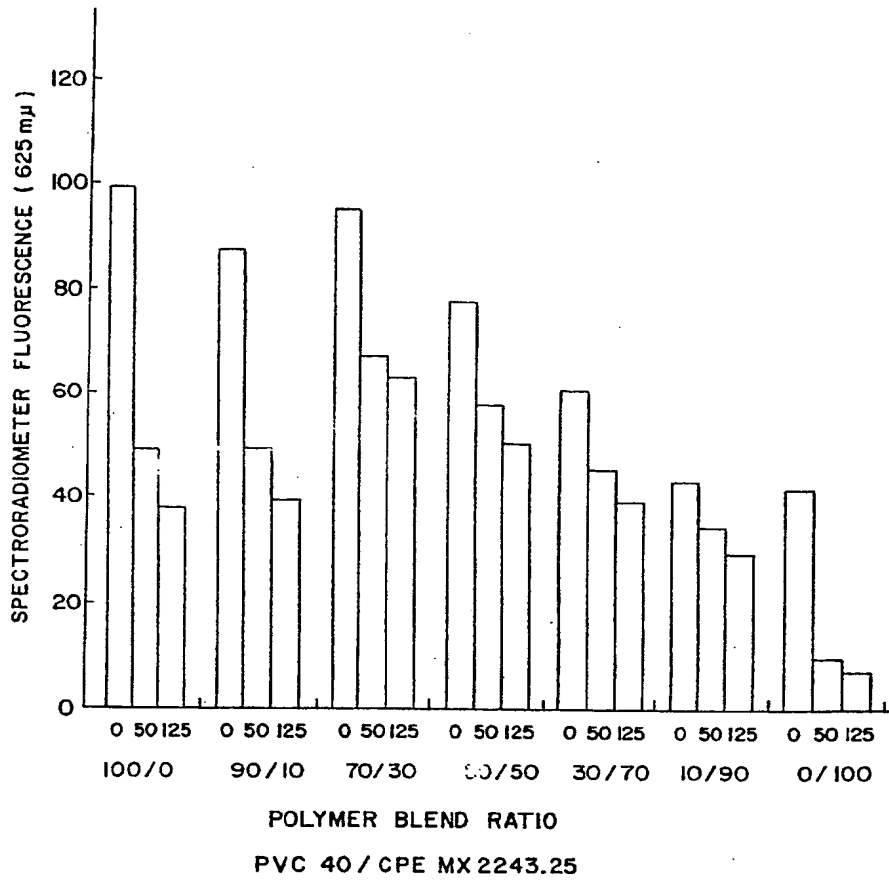
FIG_2

FLUORESCENCE DECAY VS EMMA EXPOSURE
0-50-125 THOUSAND LANGLEYS



FIG_3

FLUORESCENCE DECAY VS EMMA EXPOSURE
0-50-125 THOUSAND LANGLEYS



FIG_4